

Overload breakdown in models for photosynthesis

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Abstract

In many models of the Calvin cycle of photosynthesis it is observed that there are solutions where concentrations of key substances belonging to the cycle tend to zero at late times, a phenomenon known as overload breakdown. In this paper we prove theorems about the existence and non-existence of solutions of this type and obtain information on which concentrations tend to zero when overload breakdown occurs. As a starting point we take a model of Pettersson and Ryde-Pettersson which seems to be prone to overload breakdown and a modification of it due to Poolman which was intended to avoid this effect.

1 Introduction

Photosynthesis is one of the most important processes in biology and a variety of mathematical models have been set up in order to describe it. These have mainly been concerned with the part of photosynthesis known as the dark reactions, also known as carbon fixation or the Calvin cycle. In the simplest pictures of this process (see e.g. [1]) the substances included in the description are the five carbohydrate phosphates RuBP, PGA, DPGA, GAP and Ru5P. In [5] the properties of some models of this type were considered, together with a model which in addition includes the concentration of ATP as a variable. In [12] dynamical properties of solutions of these models and related ones were studied. It was found that for many of the models there are solutions where the concentrations become unboundedly large at late times although they remain finite on all finite time intervals (runaway solutions). The one exception is the model including ATP, for which it was shown that all solutions are globally bounded. At the same time it was shown for all the models considered that there are large classes of initial data for which the corresponding solutions are such that the concentrations of all carbohydrate phosphates tend to zero as time tends to infinity. In other words all these concentrations become arbitrarily small at late times. In [12] no biological interpretation was offered for this behaviour.

Both these phenomena, where the concentrations become arbitrarily large or small, might be taken as indications that these models are inappropriate. It suggests that it would be worthwhile to examine alternative models to see if they exhibit similar behaviour.

In this paper we study some models of the Calvin cycle which incorporate more aspects of the biology. In the simple models the five substances included are linked by reactions forming a cycle. In the models considered in what follows this simple circular topology of the reaction network is replaced by a more complicated branched one. The starting point is a model introduced by Pettersson and Ryde-Pettersson in [9]. We call this the Pettersson model. The unknowns are concentrations of substances in the chloroplast, where the Calvin cycle takes place. Most of the reactions in the model convert some of these substances into others. It also includes some transport processes, where substances are exported from the chloroplast to the surrounding cytosol and a process in which they are stored as starch in the chloroplast. It was found in [9] that for certain parameter values, corresponding to high concentrations of inorganic phosphate in the cytosol, solutions of this model can undergo a process called overload breakdown where the export of sugars cannot be maintained. Since this behaviour may be biologically unrealistic Poolman [10] introduced a new model, which we call the Poolman model, in an attempt to avoid solutions of this type. Overload breakdown corresponds to a situation where more sugar phosphates are being exported from the system than can be produced and to combat this Poolman introduced an extra reaction describing starch degradation, i.e. the production of sugar phosphates from starch. This is the only difference between the reaction networks used in the Pettersson and Poolman models. There is also a difference in the kinetics which describe the mechanisms of certain reactions. Yet another choice of kinetics, which has the advantage of simplicity, is mass action kinetics. The models obtained from the two networks by applying mass action kinetics will be called the Pettersson-MA and Poolman-MA models. For all these models it is easy to see that all solutions remain bounded, due to the conservation of the total amount of phosphate. They have no runaway solutions. In what follows we investigate under what circumstances these models with mass action kinetics admit solutions where some concentrations tend to zero at late times and to what extent these conclusions can be transferred to the original Pettersson and Poolman models.

The paper proceeds as follows. In Sect. 2 the various models are introduced and the relations between them are described. The question, which combinations of the variables in the system might tend to zero at late times is examined in Sect. 3. In other words, necessary conditions for a point on the boundary of the state space to be an ω -limit point of a positive solution are obtained. It is shown in Sect. 4 that in the case of the Pettersson-MA model there are large classes of solutions for which many concentrations converge to zero as $t \rightarrow \infty$ and it is investigated to what extent this is prevented by moving to the Poolman-MA model. The set of substances whose concentrations may tend to zero gives a new picture of the details of overload breakdown. The main results on the Pettersson-MA and Poolman-MA models are contained in Theorem

1. Sect. 5 is concerned with generalizing some of these results to the original Poolman model. Conclusions and an outlook are given in the last section.

This paper is based in part on the master's thesis of the first author [8].

2 Basic definitions

This section gives the definitions of four models of the Calvin cycle mentioned in the introduction, the Pettersson-MA, Poolman-MA, Poolman and Pettersson models. The underlying reaction network is given in Figure 1.

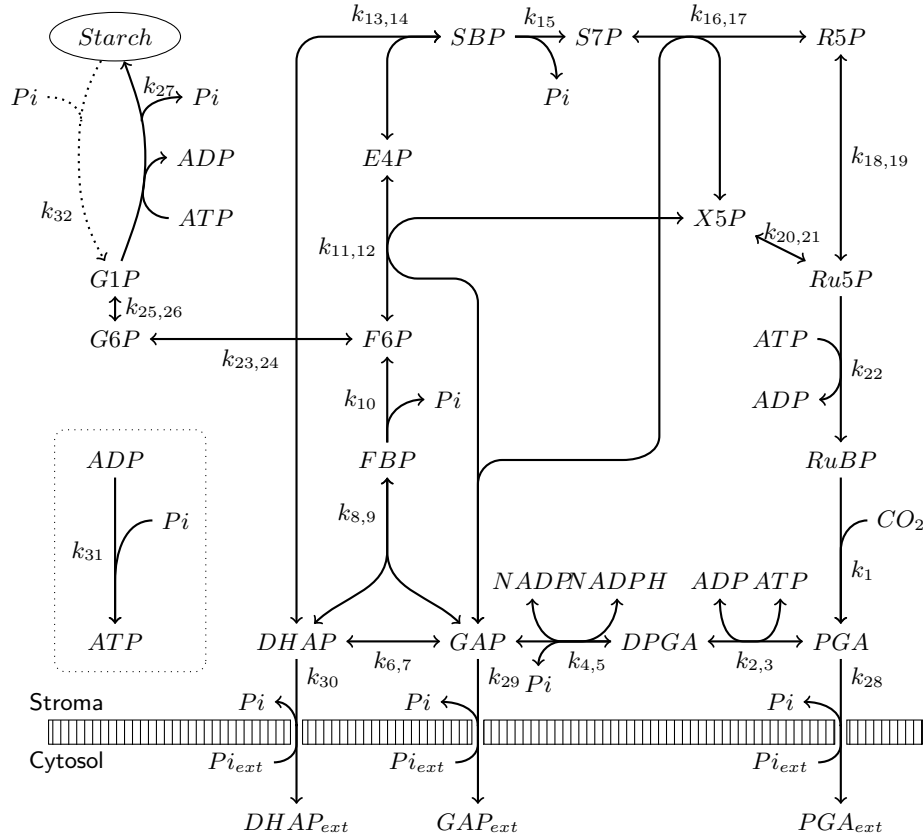


Figure 1: diagram of the network

In the case of the Pettersson model $k_{32} = 0$ and one of the reactions can be dropped. In the case of the Poolman model $k_{32} \neq 0$. The system of ordinary differential equations obtained by applying mass action kinetics in all reactions will now be presented. To our knowledge this model has not previously ap-

peared explicitly in the literature although it does occur implicitly in [4]. In that reference the author investigates the applicability of some theorems of chemical reaction network theory to this system and since the hypotheses of these theorems include mass action kinetics the only logical interpretation is that he applied these techniques to the mass action system arising from the given network. The unknowns in the system are the concentrations of RuBP, PGA, DPGA, ATP, GAP, P_i , DHAP, FBP, F6P, E4P, X5P, SBP, S7P, R5P, Ru5P, G6P and G1P. The equations are

$$\frac{dx_{RuBP}}{dt} = -k_1 x_{RuBP} + k_{22} x_{Ru5P} x_{ATP}, \quad (1)$$

$$\begin{aligned} \frac{dx_{PGA}}{dt} &= 2k_1 x_{RuBP} + k_2 x_{DPGA} (c_A - x_{ATP}) \\ &\quad - k_3 x_{PGA} x_{ATP} - k_{28} x_{PGA}, \end{aligned} \quad (2)$$

$$\begin{aligned} \frac{dx_{DPGA}}{dt} &= -k_2 x_{DPGA} (c_A - x_{ATP}) + k_3 x_{PGA} x_{ATP} \\ &\quad + k_4 x_{GAP} x_{P_i} - k_5 x_{DPGA}, \end{aligned} \quad (3)$$

$$\begin{aligned} \frac{dx_{ATP}}{dt} &= k_2 x_{DPGA} (c_A - x_{ATP}) - k_3 x_{PGA} x_{ATP} - k_{22} x_{Ru5P} x_{ATP} \\ &\quad - k_{27} x_{G1P} x_{ATP} + k_{31} x_{P_i} (c_A - x_{ATP}), \end{aligned} \quad (4)$$

$$\begin{aligned} \frac{dx_{GAP}}{dt} &= -k_4 x_{GAP} x_{P_i} + k_5 x_{DPGA} + k_6 x_{DHAP} - k_7 x_{GAP} + k_8 x_{FBP} \\ &\quad - k_9 x_{GAP} x_{DHAP} + k_{11} x_{E4P} x_{X5P} - k_{12} x_{F6P} x_{GAP} + k_{16} x_{X5P} x_{R5P} \\ &\quad - k_{17} x_{S7P} x_{GAP} - k_{29} x_{GAP}, \end{aligned} \quad (5)$$

$$\begin{aligned} \frac{dx_{P_i}}{dt} &= -k_4 x_{GAP} x_{P_i} + k_5 x_{DPGA} + k_{10} x_{FBP} + k_{15} x_{SBP} \\ &\quad + 2k_{27} x_{G1P} x_{ATP} + k_{28} x_{PGA} + k_{29} x_{GAP} + k_{30} x_{DHAP} \\ &\quad - k_{31} x_{P_i} (c_A - x_{ATP}) - k_{32} x_{P_i}, \end{aligned} \quad (6)$$

$$\begin{aligned} \frac{dx_{DHAP}}{dt} &= -k_6 x_{DHAP} + k_7 x_{GAP} + k_8 x_{FBP} - k_9 x_{GAP} x_{DHAP} \\ &\quad + k_{13} x_{SBP} - k_{14} x_{DHAP} x_{E4P} - k_{30} x_{DHAP}, \end{aligned} \quad (7)$$

$$\frac{dx_{FBP}}{dt} = -k_8 x_{FBP} + k_9 x_{GAP} x_{DHAP} - k_{10} x_{FBP}, \quad (8)$$

$$\begin{aligned} \frac{dx_{F6P}}{dt} &= k_{10} x_{FBP} + k_{11} x_{E4P} x_{X5P} - k_{12} x_{F6P} x_{GAP} \\ &\quad + k_{23} x_{G6P} - k_{24} x_{F6P}, \end{aligned} \quad (9)$$

$$\begin{aligned} \frac{dx_{E4P}}{dt} &= -k_{11} x_{E4P} x_{X5P} + k_{12} x_{F6P} x_{GAP} \\ &\quad + k_{13} x_{SBP} - k_{14} x_{DHAP} x_{E4P}, \end{aligned} \quad (10)$$

$$\begin{aligned} \frac{dx_{X5P}}{dt} &= -k_{11} x_{E4P} x_{X5P} + k_{12} x_{F6P} x_{GAP} - k_{16} x_{X5P} x_{R5P} \\ &\quad + k_{17} x_{S7P} x_{GAP} + k_{20} x_{Ru5P} - k_{21} x_{X5P}, \end{aligned} \quad (11)$$

$$\frac{dx_{SBP}}{dt} = -k_{13} x_{SBP} + k_{14} x_{DHAP} x_{E4P} - k_{15} x_{SBP}, \quad (12)$$

$$\frac{dx_{S7P}}{dt} = k_{15}x_{SBP} + k_{16}x_{X5P}x_{R5P} - k_{17}x_{S7P}x_{GAP}, \quad (13)$$

$$\frac{dx_{R5P}}{dt} = -k_{16}x_{X5P}x_{R5P} + k_{17}x_{S7P}x_{GAP} + k_{18}x_{Ru5P} - k_{19}x_{R5P}, \quad (14)$$

$$\begin{aligned} \frac{dx_{Ru5P}}{dt} = & -k_{18}x_{Ru5P} + k_{19}x_{R5P} - k_{20}x_{Ru5P} \\ & + k_{21}x_{X5P} - k_{22}x_{Ru5P}x_{ATP}, \end{aligned} \quad (15)$$

$$\frac{dx_{G6P}}{dt} = -k_{23}x_{G6P} + k_{24}x_{F6P} + k_{25}x_{G1P} - k_{26}x_{G6P}, \quad (16)$$

$$\frac{dx_{G1P}}{dt} = -k_{25}x_{G1P} + k_{26}x_{G6P} - k_{27}x_{G1P}x_{ATP} + k_{32}x_{P_i} \quad (17)$$

where x_X denotes the concentration of any substance X and the k_i are constants, the reaction constants. These are all positive with the possible exception of k_{32} . When it is zero the equations define the Pettersson-MA model and when it is positive they define the Poolman-MA model. $c_A = x_{ADP} + x_{ATP}$ is the total concentration of adenosine phosphates. It is constant in time and this fact has been used to eliminate x_{ADP} from the evolution equations. The concentrations of substances in the cytosol in the diagram of the network, which carry the subscript ‘ext’, are not included in the model. Their concentrations have been assumed fixed so that they are not dynamical variables. The same is true for CO_2 , NADP, NADPH and starch. The solutions of biological interest are those which are positive (i.e. all concentrations are positive). Solutions which are non-negative but not positive are of interest as limits of the biologically applicable ones. Solutions which start positive remain positive and those which start non-negative remain non-negative. This is a consequence of Lemma 1 in the next section. Let S denote the positive orthant in the space of concentrations and \bar{S} its closure. Then S and \bar{S} are invariant under the evolution. The total quantity of phosphate in the system is

$$\begin{aligned} c_P = & 2x_{RuBP} + x_{PGA} + 2x_{DPGA} + x_{GAP} + x_{P_i} + x_{DHAP} \\ & + 2x_{FBP} + x_{F6P} + x_{E4P} + x_{X5P} + 2x_{SBP} + x_{S7P} \\ & + x_{R5P} + x_{Ru5P} + x_{G6P} + x_{G1P} + 3x_{ATP} + 2x_{ADP}. \end{aligned} \quad (18)$$

It is conserved for biological reasons and of course it follows directly from the evolution equations that the time derivative of this quantity is zero. In particular it is a bounded function of time. Since all substances occurring in the system contain phosphate it follows that all concentrations are bounded and that solutions of the system exist globally in time.

In the original Pettersson model a distinction is made between fast reversible and slow irreversible reactions when specifying the kinetics. The irreversible reactions are $RuBP \rightarrow PGA$, $FBP \rightarrow F6P$, $SBP \rightarrow S7P$, $Ru5P \rightarrow RuBP$, $ADP + P_i \rightarrow ATP$, $G1P + ATP \rightarrow ADP + P_i$, $PGA \rightarrow P_i$, $GAP \rightarrow P_i$ and $DPGA \rightarrow P_i$. In the original Poolman model these reactions are given the same kinetics as in the Pettersson model. These kinetics are chosen on the basis of experimental data. In the Poolman model the remaining reactions are given

mass action kinetics. The evolution equations can be expressed in terms of reaction rates v_i without the kinetics being fixed. The result is

$$\frac{dx_{RuBP}}{dt} = v_{13} - v_1, \quad (19)$$

$$\frac{dx_{PGA}}{dt} = 2v_1 - v_2 - v_{PGA}, \quad (20)$$

$$\frac{dx_{DPGA}}{dt} = v_2 - v_3, \quad (21)$$

$$\frac{dx_{ATP}}{dt} = v_{16} - v_2 - v_{13} - v_{st}, \quad (22)$$

$$\frac{dx_{GAP}}{dt} = v_3 - v_4 - v_5 - v_7 - v_{10} - v_{GAP}, \quad (23)$$

$$\frac{dx_{DHAP}}{dt} = v_4 - v_5 - v_8 - v_{DHAP}, \quad (24)$$

$$\frac{dx_{FBP}}{dt} = v_5 - v_6, \quad (25)$$

$$\frac{dx_{F6P}}{dt} = v_6 - v_7 - v_{14}, \quad (26)$$

$$\frac{dx_{E4P}}{dt} = v_7 - v_8, \quad (27)$$

$$\frac{dx_{X5P}}{dt} = v_7 + v_{10} - v_{12}, \quad (28)$$

$$\frac{dx_{SBP}}{dt} = v_8 - v_9, \quad (29)$$

$$\frac{dx_{S7P}}{dt} = v_9 - v_{10}, \quad (30)$$

$$\frac{dx_{R5P}}{dt} = v_{10} - v_{11}, \quad (31)$$

$$\frac{dx_{Ru5P}}{dt} = v_{11} + v_{12} - v_{13}, \quad (32)$$

$$\frac{dx_{G6P}}{dt} = v_{14} - v_{15}, \quad (33)$$

$$\frac{dx_{G1P}}{dt} = v_{15} - v_{st} + v_{17} \quad (34)$$

$$\frac{dx_{P_i}}{dt} = v_3 + v_6 + v_9 + v_{PGA} + v_{GAP} + v_{DHAP} + 2v_{st} - v_{16} - v_{17}. \quad (35)$$

These equations are identical to those in [9] except for the fact that a rate v_{17} has been added to accommodate the degradation of starch in the Poolman model and that the equation for the concentration of inorganic phosphate has been included explicitly. In [9] this last equation was omitted since it can be computed from the other concentrations using the conservation law for the total amount of phosphate. In [9] the slow reactions correspond to the v_i with $i = 1, 6, 9, 13, 16$ and the rates of the export reactions v_{PGA} , v_{GAP} and v_{DHAP} . Poolman also

takes the additional reaction he introduces to be a slow reaction, with rate [10]

$$v_{17} = \frac{V_{17}x_{P_i}}{x_{P_i} + K_m(1 + K_{i17}^{-1}x_{G1P})}. \quad (36)$$

The expressions for the v_i in the Pettersson-MA and Poolman-MA models can be read off by comparing these equations with the evolution equations for those models given earlier. This gives the expressions for the v_i in the Poolman model in the case of the fast reactions. The rates of the slow reactions in the Poolman model apart from v_{17} are taken from those in the Pettersson model and are as follows

$$v_1 = \frac{V_1x_{RuBP}}{x_{RuBP} + M_1}, \quad (37)$$

$$v_6 = \frac{V_6x_{FBP}}{x_{FBP} + K_{m6}(1 + K_{i61}^{-1}x_{F6P} + K_{i62}^{-1}x_{P_i})}, \quad (38)$$

$$v_9 = \frac{V_6x_{SBP}}{x_{SBP} + K_{m9}(1 + K_{i9}^{-1}x_{P_i})}, \quad (39)$$

$$v_{13} = \frac{V_{13}x_{Ru5P}x_{ATP}}{M_{13}}, \quad (40)$$

$$v_{16} = \frac{V_{16}x_{ADP}x_{P_i}}{(x_{ADP} + K_{m161})(x_{P_i} + K_{m162})}, \quad (41)$$

$$v_{PGA} = \frac{V_{ex}x_{PGA}}{NK_{PGA}}, \quad (42)$$

$$v_{GAP} = \frac{V_{ex}x_{GAP}}{NK_{GAP}}, \quad (43)$$

$$v_{DHAP} = \frac{V_{ex}x_{DHAP}}{NK_{DHAP}}, \quad (44)$$

$$v_{st} = \frac{V_{st}x_{G1P}x_{ATP}}{(x_{G1P} + K_{mst1})M_{st}}. \quad (45)$$

Here

$$M_1 = K_{m1} \left(1 + \frac{x_{PGA}}{K_{i11}} + \frac{x_{FBP}}{K_{i12}} + \frac{x_{SBP}}{K_{i13}} + \frac{x_{P_i}}{K_{i14}} + \frac{x_{NADPH}}{K_{i14}} \right), \quad (46)$$

$$M_{13} = [x_{Ru5P} + K_{m131}(1 + K_{i131}^{-1}x_{PGA} + K_{i132}^{-1}x_{RuBP} + K_{i132}^{-1}x_{P_i})] \\ \times [x_{ATP}(1 + K_{i134}^{-1}x_{ADP}) + K_{m132}(1 + K_{i135}^{-1}x_{ADP})], \quad (47)$$

$$M_{st} = (1 + K_{ist}^{-1}x_{ADP})(x_{ATP} + K_{mst2}(1 + K_{mst2}x_{P_i} \\ \times (K_{ast1}x_{PGA} + K_{ast2}x_{F6P} + K_{ast3}x_{FBP})^{-1}), \quad (48)$$

$$N = 1 + (1 + x_{P_{ext}}^{-1}) \left(\frac{x_{P_i}}{K_{P_i}} + \frac{x_{PGA}}{K_{PGA}} + \frac{x_{GAP}}{K_{GAP}} + \frac{x_{DHAP}}{K_{DHAP}} \right). \quad (49)$$

It been pointed out in [2] that the expression for v_{st} in [9] is incorrect and in the expression for M_{st} given above we have used the replacement proposed in [2]. In the original Pettersson model the fast reactions are assumed to be

at equilibrium which leads to a system of differential-algebraic equations. The latter model will not be treated further in the present paper.

In the Calvin cycle most reactions conserve the number of carbon atoms. There are, however, some inflow and outflow reactions for which the number of carbon atoms which are in the chloroplast and not stored as starch is not conserved. Hence the total number of carbon atoms in the substances included in the model is not conserved. It is nevertheless useful to consider the following small modification of the total number of carbon atoms. Define a quantity L_1 by

$$\begin{aligned} 5L_1 = & 5x_{RuBP} + \frac{5}{2}x_{PGA} + 3x_{DPGA} + 3x_{GAP} + 3x_{DHAP} + 6x_{FBP} \\ & + 6x_{F6P} + 4x_{E4P} + 5x_{X5P} + 7x_{SBP} + 7x_{S7P} + 5x_{R5P} + 5x_{Ru5P} \\ & + 6x_{G6P} + 6x_{G1P}. \end{aligned} \quad (50)$$

This is inspired by a Lyapunov function constructed by trial and error in [12] which is related in a similar way to the total number of carbon atoms. Its time derivative is given by

$$\begin{aligned} \frac{d}{dt}(5L_1) = & \left(\frac{1}{2}k_3x_{ATP} - \frac{5}{2}k_{28} \right) x_{PGA} - \frac{1}{2}k_2x_{DPGA}x_{ADP} \\ & - 6k_{27}x_{ATP}x_{G1P} - 3k_{29}x_{GAP} - 3k_{30}x_{DHAP} + k_{32}x_{P_i} \end{aligned} \quad (51)$$

for the Pettersson-MA and Poolman-MA models.

In the Pettersson-MA model if it is assumed that the parameters are such that $k_3c_A \leq 5k_{28}$ then L_1 is a Lyapunov function and it is strictly decreasing for positive solutions. It follows that in this case all ω -limit points of a positive solution are on the boundary of S and that, in particular, there are no positive stationary solutions. This parameter restriction is the direct analogue of one found to play a role in the dynamics of the simple model including ATP considered in Section 6 of [12].

3 Potential ω -limit points

In this section information will be obtained on the location of ω -limit points of positive solutions of the Pettersson-MA and Poolman-MA systems. Many of the arguments use the following simple lemma.

Lemma 1 Consider an ordinary differential equation of the form $\dot{u}(t) = -a(t)u(t) + b(t)$ where a and b are non-negative continuous functions and a solution $u(t)$ which satisfies $u(t_0) \geq 0$ for some t_0 . Then if $b(t_1) > 0$ for some $t_1 > t_0$ it follows that $u(t_1) > 0$.

Proof Suppose first that $u(t_0) > 0$. Then u remains positive for t slightly larger than t_0 and as long as it does so the equation can be rewritten as $\frac{d}{dt}(\log u) = -a + \frac{b}{u}$. Thus $\frac{d}{dt}(\log u) \geq -a$ and $\log u$ cannot tend to $-\infty$ in finite time. Hence u cannot tend to zero in finite time and u remains strictly positive. It then follows using the continuous dependence of solutions on initial data that

if u starts non-negative it stays non-negative. Now suppose there were a time $t_1 > t_0$ with $u(t_1) = 0$ and $b(t_1) > 0$. Then $\dot{u}(t_1) > 0$. This implies that $u(t)$ is negative for t slightly less than t_1 , in contradiction to what has already been proved. This completes the proof of the lemma.

It is also often useful to apply the contrapositive statement: if $u(t_1) = 0$ then $b(t_1) = 0$. In the applications of this lemma below u will be one of the concentrations in a photosynthesis model and the functions a and b are obtained by setting the other concentrations to their values in a fixed non-negative solution.

The strategy is now to successively obtain restrictions on the position of an ω -limit point of a positive solution.

Lemma 2 At an ω -limit point of a positive solution of the Pettersson-MA or Poolman-MA model on the boundary of S the concentrations of the following substances vanish: RuBP, PGA, DPGA, GAP, DHAP, FBP, SBP.

Proof The proof consists of repeated applications of Lemma 1 to the solution of the dynamical system passing through the ω -limit point being considered. Consider an ω -limit point where $x_{GAP} > 0$. Then the evolution equation for x_{P_i} shows that this quantity is positive at the given point. In the same way the concentrations of the following quantities are positive: DHAP, FBP, F6P, E4P, X5P, SBP, S7P, R5P, Ru5P, G6P, G1P, ATP, RuBP, PGA, DPGA. This implies that the ω -limit point is in the interior of S , contrary to the assumptions of the lemma. Thus it follows that in fact $x_{GAP} = 0$. The evolution equation for x_{GAP} then implies that the concentrations of DPGA, DHAP and FBP vanish. The evolution equation for x_{DHAP} then implies that the concentration of SBP vanishes. To proceed further we need to distinguish between the cases where the concentration of ATP is non-zero or zero at the given point. In the first case we can conclude successively that the concentrations of PGA and RuBP vanish, completing the proof. In the second case $x_{P_i} = 0$ and the evolution equation for x_{P_i} implies that $x_{PGA} = 0$. It then follows as in the first case that $x_{RuBP} = 0$.

Lemma 3 At an ω -limit point of a positive solution of the Pettersson-MA or Poolman-MA model on the boundary of S the concentrations of $X5P$, $R5P$ and $Ru5P$ vanish.

Proof The evolution equations for $X5P$, $R5P$ and $Ru5P$ show that the concentrations of all three substances vanish at an ω -limit point of a stationary solution if and only if any one of them does. However supposing that none of them vanishes leads to a contradiction in the evolution equation for GAP .

Lemma 4 At an ω -limit point on the boundary of S of a positive solution of the Pettersson-MA model with $k_3c_A \leq 5k_{28}$ either the concentrations of $G1P$, $G6P$ and $F6P$ vanish or all three are non-vanishing and $x_{ATP} = x_{P_i} = 0$.

Proof In the Pettersson-MA and Poolman-MA models the evolution equations for $G1P$, $G6P$ and $F6P$ show that the concentrations of all three substances vanish at an ω -limit point of a positive solution if and only if any one of them does. In the case of the Pettersson-MA model with $k_3c_A \leq 5k_{28}$ it follows from the expression for the time derivative of L_1 that $x_{ATP}x_{G1P}$ vanishes at any ω -limit point. If $x_{G1P} \neq 0$ at that point then $x_{ATP} = 0$ there. It follows that $x_{P_i} = 0$ at that point

Lemma 5 At an ω -limit point on the boundary of S of a positive solution of the Poolman-MA model either the concentrations of all three hexoses $G1P$, $G6P$ and $F6P$ vanish or none of them does so. One of the following three cases holds:

1. $x_{P_i} = 0$, all hexose concentrations are zero or
2. $x_{P_i} = 0$, $x_{ATP} = 0$, all hexose concentrations are non-zero or
3. $x_{P_i} \neq 0$, $x_{ATP} \neq 0$, all hexose concentrations are non-zero.

Proof The first statement is part of Lemma 4. When $x_{G1P} = 0$ at an ω -limit point on the boundary it follows from the evolution equation for x_{G1P} that $x_{P_i} = 0$. This is case 1. Otherwise all hexose concentrations are non-zero. In that case if $x_{P_i} = 0$ the evolution equation for x_{P_i} shows that $x_{ATP} = 0$. On the other hand if $x_{ATP} = 0$ the evolution equation for $x_{ATP} = 0$ shows that $x_{P_i} = 0$.

Any stationary solution on the boundary satisfies the conditions derived above for ω -limit points. In the Petterson-MA model a stationary solution with non-vanishing hexose concentrations satisfies $x_{P_i} = 0$ and $x_{ATP} = 0$ without the restriction on the parameters occurring in Lemma 4. If, on the other hand, the concentrations of the hexoses vanish then the conditions for stationary solutions reduce to the condition that either $x_{P_i} = 0$ or $x_{ADP} = 0$. Given the fact that the concentrations of x_{E4P} and x_{S7P} can be prescribed freely we see that there are two three-parameter families of stationary solutions which meet at the point where both x_{P_i} and x_{ADP} are zero. In the case that the concentrations of the hexoses do not vanish we get a three-parameter family of stationary solutions satisfying the conditions $k_{23}x_{G6P} = k_{24}x_{F6P}$ and $k_{25}x_{G1P} = k_{26}x_{G6P}$. Consider now the Poolman-MA model. When $x_{P_i} = 0$ the two systems agree and so the set of stationary solutions is identical. It remains to consider the possibility that there are stationary solutions of the Poolman-MA model with $x_{P_i} \neq 0$. They would belong to case 3. of Lemma 5 and satisfy the relation $k_{31}(c_A - x_{ATP}) = k_{32}$. Substituting this into the equation for x_{P_i} gives a contradiction and so stationary solutions of this type do not exist.

4 Linearization about the ω -limit points

In Lemma 2 and Lemma 3 a set was identified, call it Z , where any ω -limit point of a solution of the Petterson-MA model or the Poolman-MA model must lie. Consider now the linearization of the full model about a point of Z . The linearized quantity for a given substance is denoted by a y with the name of that substrate as a subscript. The aim is to find a block upper triangular form for the linearization, so as to obtain information about its eigenvalues. The linearized equation for FBP depends only on that substance and so can be split off, contributing a negative eigenvalue. At a general point of Z it is difficult to proceed further with this strategy. The simplest points about which to linearize

are the points z_0 where all carbohydrate concentrations and x_{P_i} are zero. Denote the concentration of ATP at the point z_0 by a . The linearization is

$$\frac{dy_{RuBP}}{dt} = -k_1 y_{RuBP} + k_{22} a y_{Ru5P}, \quad (52)$$

$$\frac{dy_{PGA}}{dt} = 2k_1 y_{RuBP} + k_2 (c_A - a) y_{DPGA} - (k_3 a + k_{28}) y_{PGA}, \quad (53)$$

$$\frac{dy_{DPGA}}{dt} = -[k_2 (c_A - a) + k_5] y_{DPGA} + k_3 a y_{PGA}, \quad (54)$$

$$\begin{aligned} \frac{dy_{ATP}}{dt} &= k_2 (c_A - a) y_{DPGA} - k_3 a y_{PGA} - k_{22} a y_{Ru5P} \\ &\quad - k_{27} a y_{G1P} + k_{31} (c_A - a) y_{P_i}, \end{aligned} \quad (55)$$

$$\frac{dy_{GAP}}{dt} = k_5 y_{DPGA} + k_6 y_{DHAP} - k_7 y_{GAP} - k_{29} y_{GAP}, \quad (56)$$

$$\begin{aligned} \frac{dy_{P_i}}{dt} &= k_5 y_{DPGA} + k_{15} y_{SBP} + 2k_{27} a y_{G1P} + k_{28} y_{PGA} \\ &\quad + k_{29} y_{GAP} + k_{30} y_{DHAP} - k_{31} (c_A - a) y_{P_i} - k_{32} y_{P_i}, \end{aligned} \quad (57)$$

$$\frac{dy_{DHAP}}{dt} = -k_6 y_{DHAP} + k_7 y_{GAP} + k_{13} y_{SBP} - k_{30} y_{DHAP}, \quad (58)$$

$$\frac{dy_{F6P}}{dt} = k_{23} y_{G6P} - k_{24} y_{F6P}, \quad (59)$$

$$\frac{dy_{E4P}}{dt} = k_{13} y_{SBP}, \quad (60)$$

$$\frac{dy_{X5P}}{dt} = k_{20} y_{Ru5P} - k_{21} y_{X5P}, \quad (61)$$

$$\frac{dy_{SBP}}{dt} = -(k_{13} + k_{15}) y_{SBP}, \quad (62)$$

$$\frac{dy_{S7P}}{dt} = k_{15} y_{SBP}, \quad (63)$$

$$\frac{dy_{R5P}}{dt} = k_{18} y_{Ru5P} - k_{19} y_{R5P}, \quad (64)$$

$$\begin{aligned} \frac{dy_{Ru5P}}{dt} &= -k_{18} y_{Ru5P} + k_{19} y_{R5P} - k_{20} y_{Ru5P} \\ &\quad + k_{21} y_{X5P} - k_{22} a y_{Ru5P}, \end{aligned} \quad (65)$$

$$\frac{dy_{G6P}}{dt} = -k_{23} y_{G6P} + k_{24} y_{F6P} + k_{25} y_{G1P} - k_{26} y_{G6P}, \quad (66)$$

$$\frac{dy_{G1P}}{dt} = -k_{25} y_{G1P} + k_{26} y_{G6P} - k_{27} a y_{G1P} + k_{32} y_{P_i} \quad (67)$$

Here the quantity y_{FBP} has been set to zero and its evolution equations omitted since it plays no role in what follows.

Lemma 6 Let L be the linearization of the right hand side of the equations of Pettersson-MA model at a point of the form z_0 . Then all eigenvalues of L have non-positive real part and at most four have zero real part. The multiplicity of the eigenvalue zero is four when $x_{ATP} = c_A$ and three otherwise.

Proof The equation for SBP is decoupled from the others and contributes a

negative eigenvalue. The rows and columns corresponding to this variable can be discarded. The variables E4P and S7P can then be treated in the same way, both contributing zero eigenvalues. Consider next the evolution equations for the variables y_{G1P} , y_{G6P} and y_{F6P} . They form a closed system and define a submatrix which can be analysed on its own. The trace and determinant of this block are negative. The characteristic polynomial can easily be computed and the Routh-Hurwitz criterion [3] shows that all eigenvalues have negative real parts. The equations for y_{X5P} , y_{Ru5P} and y_{R5P} can be treated in exactly the same way. Once this has been done the quantity y_{RuBP} can be handled in the same way as the variables for FBP and SBP. The quantities y_{PGA} and y_{DPGA} define a 2 by 2 block which has negative trace and positive determinant. It contributes eigenvalues with negative real parts. Next y_{GAP} and y_{DHAP} can be treated together. They also contribute a 2 by 2 matrix with negative trace and positive determinant and therefore two eigenvalues with negative real parts. The equation for y_{P_i} is now decoupled and gives the eigenvalue $-k_{31}(c_A - a)$, where a is the concentration of ATP at the given point. Finally y_{P_i} contributes a zero eigenvalue. This completes the proof.

Lemma 7 Let L be the linearization of the right hand side of the equations of the Poolman-MA model at the point z_0 with $x_{ADP} = 0$. For k_{32} sufficiently small there is one eigenvalue with positive real part, three zero eigenvalues and all the other eigenvalues have negative real part

Proof The methods in the proof of Lemma 6 can be used in a very similar way to eliminate all the variables except y_{G1P} , y_{G6P} , y_{F6P} , y_{ATP} and y_{P_i} from consideration in the case $k_{32} \neq 0$. In the remaining system of five equations y_{ATP} does not occur on the right hand side and so can also be eliminated, producing a further zero eigenvalue. To complete the argument the eigenvalues of a four by four matrix must be examined. They depend continuously on the parameter k_{32} . When $k_{32} = 0$ three of the eigenvalues have negative real parts according to Lemma 6. These eigenvalues retain this property for sufficiently small values of k_{32} . In this regime the sign of the remaining eigenvalue, which is real, is the opposite of that of the determinant. The determinant is $-k_{24}k_{26}k_{27}k_{32}c_A$, which is negative.

Lemma 6 and Lemma 7 can be used in combination with the reduction theorem (see [7], Theorem 5.4) to obtain results on positive solutions of the nonlinear equations which start close to a point of the form z_0 . Consider first the case of the Petterson-MA model with $x_{ATP} = c_A$. The centre manifold is four-dimensional and is given by the vanishing of all variables except x_{E4P} , x_{S7P} , x_{ATP} and x_{P_i} . The restriction of the system to that manifold is the product of a trivial system for x_{E4P} and x_{S7P} with a two-dimensional system which is easily analysed. The conclusion is that solutions which start close to z_0 have the property that all concentrations converge to limits as $t \rightarrow \infty$. Generically the limits of x_{E4P} and x_{S7P} are strictly positive and precisely one of the limiting concentrations x_{ADP} and x_{P_i} is positive. If instead $x_{ATP} < c_A$ at z_0 then the centre manifold is three-dimensional. Again all concentrations tend to limits, with the limit of x_{P_i} being zero.

In the case of the Poolman-MA model and the point of the form z_0 with

$x_{ADP} = 0$ there is a one-dimensional unstable manifold and generic solutions starting close to z_0 do not stay close to z_0 . Thus z_0 is stable for the Pettersson-MA model and passing to the Poolman-MA model destabilises it. The production of sugar from starch in the Poolman-MA model means that there is no direct analogue of the argument which was used to show that the function L_1 is a Lyapunov function for the Pettersson-MA model for certain values of the parameters. Instead it is possible to identify a parameter regime where $-L_1$ is a Lyapunov function.

The total amount of phosphate can be written as the sum of the amount contained in the adenosine phosphates, the amount of inorganic phosphate and the rest $c_P = c_A + P_R + x_{P_i}$. For a positive solution the constant $c_1 = c_P - c_A$ is positive. The quantity P_R can be bounded in terms of L_1 , counting the carbon atoms, with the result that $P_R \leq 10L_1$. Hence $x_{P_i} \geq c_1 - 10L_1$. It follows that

$$\frac{dL_1}{dt} \geq 6k_{32}x_{P_i} - c_2L_1 \quad (68)$$

where c_2 is a constant which depends only on the reaction constants and the total amount of adenosine phosphates. Hence

$$\frac{dL_1}{dt} \geq 6k_{32}(c_1 - 10L_1) - c_2L_1 = 6k_{32}[c_1 - (10 + c_2/(6k_{32}))L_1]. \quad (69)$$

This quantity is positive when $c_1 - (10 + c_2/(6k_{32})) > 0$. Let $m = \frac{6k_{32}c_1}{60k_{32} + c_2}$. Then whenever L_1 is less than m its time derivative is positive. It follows that L_1 is eventually at least m . In particular, it cannot tend to zero for $t \rightarrow \infty$. The latter fact follows from the computations of the previous section but here an additional quantitative lower bound is obtained for the concentrations of the sugar phosphates at late times. It can be concluded that

$$\liminf_{t \rightarrow \infty} (4x_{E4P} + 5x_{X5P} + 6x_{G1P} + 6x_{G6P} + 6x_{F6P}) \geq m. \quad (70)$$

The main results of this section will be summed up in a theorem:

Theorem 1 There is a non-empty open set of positive initial data for which the corresponding solutions of the Pettersson-MA model converge to the boundary of S as $t \rightarrow \infty$. They include all data for which the concentrations of all carbohydrate phosphates and inorganic phosphate are bounded by a sufficiently small constant ϵ . In the latter case the concentrations of all carbohydrate phosphates except E4P and S7P tend to zero while x_{E4P} and x_{S7P} remain small as $t \rightarrow \infty$. On the other hand, the solutions of the Poolman-MA model corresponding to these data do not have the property that the concentrations of all carbohydrate phosphates remain smaller than a constant $\delta > 0$ for a suitable choice of ϵ .

5 The Poolman model

The original model of Poolman uses kinetics which are not mass action. In this section we investigate which of the results for the Poolman-MA model have

analogues in this case. The total amount of phosphate is conserved and this can be derived from the evolution equations independent of the kinetics given above together with the fact that $(d/dt)(x_{ADP}) = -(d/dt)(x_{ATP})$. Lemma 1 can be applied to this model in exactly the same way as it was applied to the Poolman-MA model. For all that is important in that context are the signs (positive, negative or zero) of the reaction rates when certain concentrations are zero or non-zero. These relations are not changed when the mass action kinetics are replaced by the more complicated kinetics in the original model. The modulation occurs because the reaction rates are multiplied by positive factors depending on the concentrations of other substances. It can be further concluded that the analogues of Lemma 2 and Lemma 3 hold for the Poolman system. The time derivative of L_1 is given by

$$\frac{d}{dt}(5L_1) = \frac{1}{2}v_2 - \frac{5}{2}v_{PGA} - 3v_{GAP} - 3v_{DHAP} - 6v_{st} + 6v_{17}. \quad (71)$$

The manifestly positive term on the right hand side of this equation is given by $6v_{17} = 6k_{32}x_{P_i}$. In order to show that the estimate obtained in the case of the Poolman-MA model extends to the Poolman model it is enough to obtain lower bounds for all the other terms on the right hand side of the equations by negative multiples of L_1 . The quantity v_2 is a combination of two mass action terms and there is nothing new to do. The remaining terms admit the desired type of bound.

6 Conclusions and outlook

In this paper information has been obtained about the dynamics of some models for the Calvin cycle of photosynthesis. It was shown for the Pettersson-MA model that if the reaction constant determining the rate of conversion of PGA to DPGA is small enough compared to that determining the rate of export of PGA from the chloroplast then the concentration of some sugar phosphate must attain arbitrarily small values at late times. In particular for these parameter values the model admits no positive stationary solutions. This is a manifestation of the phenomenon of overload breakdown. It was further shown that under these circumstances all sugar phosphate concentrations except those of E4P, S7P, G1P, G6P and F6P tend to zero for $t \rightarrow \infty$. For initial data where the initial concentrations of x_{P_i} , x_{E4P} and x_{S7P} are sufficiently small all concentrations tend to limits at late times and for generic data of this type the limits of the concentrations of E4P and S7P are not zero. In contrast it was shown that for the Poolman-MA model for generic data with x_{P_i} , x_{E4P} , x_{S7P} and x_{ATP} small it is not the case that these quantities stay small. Thus, in accordance with the original motivation, the regime of overload breakdown is destabilized by the additional term introduced by Poolman. This instability is also present in the original Poolman model.

It would be possible to introduce a hybrid model with the network of Poolman and the kinetics as in the Pettersson model. It might be possible to obtain

the Pettersson model as a singular limit of this hybrid model but the details of how to do this in a mathematically rigorous way remain to be worked out. There are a number of other interesting open questions concerning these models. Does the Poolman model (or the Poolman-MA model) have a positive stationary solution for some values of the parameters? Numerical simulations in [10] indicate that there can be two stable positive stationary solutions which exhibit hysteresis when the parameter V_{16} , which here represents the intensity of light, is varied. Compare also the discussion in [11]. Does the Pettersson model (or the Pettersson-MA model) have a positive stationary solution for some values of the parameters? Numerical simulations in [9] indicate that this is the case and that there can be one stable and one unstable solution. There are, however, no mathematical proofs that these features occur. To obtain a positive answer to one of these questions concerning the existence of stationary solutions it would suffice to show that in the case being considered positive solutions can have no ω -limit points on the boundary of S and for that it might suffice to linearize about stationary points on the boundary more general than those handled in this paper. Beyond the question of the existence of positive stationary solutions there are the questions of their multiplicity and stability. The analogous questions for the simple model including ATP considered in [5] and [12] are partly open. There are also many other models for the Calvin cycle in the literature and it would be desirable to do a careful mathematical study of their solutions. This is particularly relevant since several errors in the literature have been discovered which had gone uncorrected for many years [6], [2].

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